

## New Insights into Prebiotic Chemistry from Old Archived Miller Extracts

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Following the discovery of an archived set of samples from Stanley Miller's early experiments, analyses were undertaken to better understand the diversity of compounds produced from electric discharges acting on reducing gas mixtures (Johnson et al. 2008; Parker et al. 2010; 2011). The paper chromatography methods that Miller used in the 1950s were only capable of detecting a few amino acids and were unable to provide substantial quantitative data relative to today's techniques. Current analytical techniques are much more sensitive and selective, and are capable of precisely quantifying a much larger range of amino acids and their enantiomeric abundances.

In one study, preserved dried samples produced by Miller using a lesser-known volcanic apparatus which differed from Miller's classic apparatus in that it utilized an aspirator that injected steam into the electric discharge chamber, simulating a volcanic eruption. The volcanic apparatus produced a wider variety of amino acids than the classic configuration (Johnson et al. 2008). Prebiotic compounds synthesized in these environments may have locally accumulated where they could have undergone further processing.

An additional preserved set of samples from an experiment conducted in 1958 were also found in Miller's archived collection. These samples which had been generated using a mixture of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>S and CO<sub>2</sub> were collected, catalogued, and stored by Miller, but for unknown reasons were never studied. In our analyses (Parker et al. 2010; 2011), a total of 23 amino acids and 4 amines, including 7 organosulfur compounds, were detected in these samples. The major amino acids with chiral centers are racemic within the accuracy of the measurements, indicating that they are not contaminants introduced during sample storage. This experiment marks the first synthesis of sulfur amino acids from spark discharge experiments designed to imitate primordial environments. The relative yield of some amino acids, in particular the isomers of aminobutyric acid, are the highest ever found in a spark discharge experiment.

The simulated primordial conditions used by Miller in these experiments may serve as a model for early volcanic plume chemistry and provide insight to the possible roles such plumes may have played in abiotic organic synthesis. Additionally, the overall abundances of the synthesized amino acids in the presence of H<sub>2</sub>S are very similar to the abundances found in some carbonaceous meteorites, suggesting that H<sub>2</sub>S may have played an important role in prebiotic reactions in early solar system environments.

Although experiments using a variety of gases as components of the primordial Earth's atmospheric composition and a spark discharge apparatus configured according to Miller's original or volcanic design can be readily carried out, the unique opportunity to investigate samples prepared by the pioneer in abiotic synthesis using state of the art analytical methods is of considerable historic interest.

### References

Johnson AP et al. (2008) The Miller Volcanic Spark Discharge Experiment. *Science* 322: 404.

Parker ET, et al. (2010) Prebiotic Synthesis of Methionine and Other Sulfur-Containing Organic Compounds on the Primitive Earth: A Contemporary Reassessment of an Unpublished 1958 Stanley Miller Experiment. *Orig Life Evol Biosph* on line: DOI 10.1007/s11084-010-9228-8.

Parker ET, et al. (2011) Primordial Synthesis of Amines and Amino Acids in a 1958 Miller H<sub>2</sub>S-rich Spark Discharge Experiment. *Proc. Natl. Acad. Sci. USA*.